

- I. THE SPARK-IN-FLAME METHOD OF SPECTROGRAPHIC ANALYSIS
- II. EQUIVALENT CHEMICAL BONDS FORMED BY s, p, AND d EIGENFUNCTIONS
- III. THE CRYSTAL STRUCTURE OF SULFANITE

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# THE SPARK-IN-FLAME METHOD OF SPECTROGRAPHIC ANALYSIS AND A STUDY OF THE MUTUAL EFFECTS OF ELEMENTS ON ONE ANOTHER'S EMISSION<sup>1</sup>

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## Introduction

In recent years the development of methods for the use of the spectrograph as an instrument for the quantitative as well as qualitative chemical determination of elements has proceeded to such an extent that they may now be regarded as suitable for application to many microchemical problems. While spectrographic methods cannot in general compete with ordinary chemical quantitative analysis in point of accuracy, they possess two important advantages which make them of great value in many special cases. These are great sensitivity, which permits of the semi-quantitative estimation of amounts of material too small to be analyzed by other methods, and the great rapidity with which an analysis can be conducted. For details of procedure, accuracy of estimation, etc., the reader is referred to the literature.<sup>2</sup>

The three principal means of exciting emission spectra which have been used in quantitative analysis are the electric arc, the spark and the flame. The arc and spark methods combine the advantages of a high and to some extent controllable excitation with certain drawbacks. While the high

<sup>1</sup> Original manuscript received August 19, 1931.

<sup>2</sup> F. Löwe, "Handbuch der Physik," 21, 663 (1929); H. Lundegårdh, "Die quantitative Spektralanalyse der Elemente," G. Fischer, Jena, 1929; Eugen Schweitzer, *Z. anorg. Chem.*, 164, 127 (1927); Walter Gerlach, *ibid.*, 142, 383 (1925); A. de Gramont, *Bull. soc. chim.*, 33, 1693 (1923).

excitation makes the method applicable to a large number of elements, and gives a great sensitivity, the difficulty of uniformly introducing representative samples of the material to be analyzed into the spark or arc gases, and the fact that the emission of one element is not independent of the other elements present, lead to some difficulties. These do not seem to be serious in the cases to which the arc and spark methods are usually applied, that is, in the estimation of traces of impurity in a large and nearly constant amount of some other substance, but they impose serious limitations in case that all of the substances in the unknown samples vary largely in relative amounts. The flame method, while very reproducible and nearly free from the objections just cited,<sup>2</sup> is limited in applicability to those few elements which have relatively low excitation potentials.

#### Purpose of the Investigation.—

It was the object of the work here described to devise a method of spectroscopic analysis which would retain the advantage of the flame method but overcome some of its limitations by allowing a higher excitation. It was further proposed to study the mutual effects of some elements on each other's emission with a view toward finding conditions under which these are small, so that unknown samples containing several elements might be analyzed without extensive calibration experiments.

#### Description of Method and Apparatus

**The Method.**—After some preliminary experiments the following method was found promising. The difficulties inherent in the ordinary spark methods of vaporizing representative portions of the sample to be analyzed were overcome by atomizing solutions of the sample into a hot flame, in the customary way. The excitation in the resulting gases was then increased by passing through them a condensed discharge.

**The Burner and Atomizer.**—Figure 1, which represents the burner and atomizer, is self-explanatory. All parts were of Pyrex glass except the jet admitting gas into the

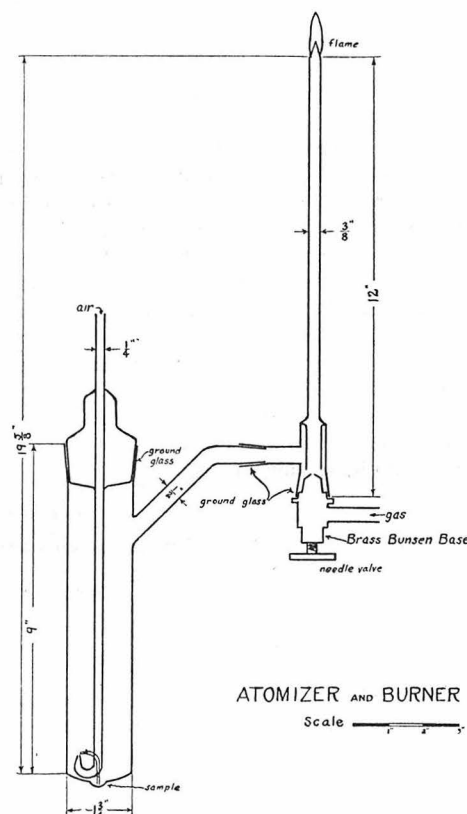


Fig. 1.—Atomizer and burner used for introduction of sample into flame.

burner, which was of brass. The design was such as to yield a steady flame and to introduce as large a quantity of solution as possible into the flame gases in finely divided drops. Any large drops produced by the spray deposit on the walls of the atomizer vessel and run back quickly, reducing the volume of solution necessary for an analysis to about 3 cc.

**The Spark.**—The electrical circuit is shown in Fig. 2. The transformer finally used was a 2 k.v.a. American transformer operating on 220 volts and yielding 25,000 volts in the secondary. With this equipment an exposure time of one minute was usually sufficient. A smaller transformer gave nearly as good results with a longer exposure.

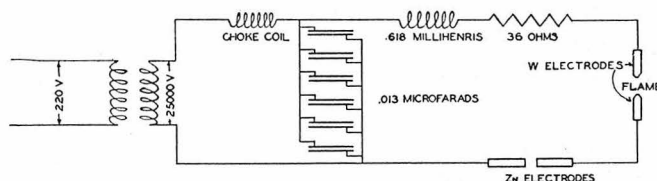


Fig. 2.—Electrical circuit for production of spark-in-flame.

The condenser consisted of  $30.5 \times 35.6$  cm. plates of heavy window glass on both sides of which  $25.4 \times 30.5$  cm. sheets of copper foil were cemented with shellac. Six plates were used and the capacity measured by a comparison method was found to be 0.013 microfarad. The inductance consisted of copper wire wound on three Pyrex glass cylinders covered with friction tape. The calculated inductance was 0.618 millihenris. With the combination of inductance and capacity given, the air lines were eliminated in the spark, and the intensity of the general background was not disturbing.

It will be noted in the diagram that an auxiliary spark gap and a fixed resistance were included in the secondary circuit. The former was found desirable since in its absence breakdown occurs at a very low potential due to the high conductivity of the flame gases. The latter serve to minimize variations due to changes in the conductivity of the flame when varying amounts of elements of low ionization potential were introduced into it, as shown in Table I.

TABLE I  
EFFECT OF RESISTANCE WIRE, IN SERIES WITH SPARK, ON SECONDARY CURRENT

Solution used for sample	Secondary current	
	Without resistance wire	With 8' 4" res. wire (54 ohms)
Distilled water	3.05	1.58
2 Molal NaCl	1.3	1.5

**The Flame.**—The fuel in the flame was hydrogen gas saturated with acetone vapor, which gave a very stable flame little affected by the introduction of large amounts of foreign substances. The city gas available is a natural gas and was found quite unsuitable since it burns with a very unstable flame. It is probable, however, that most types of manufactured city gas would work satisfactorily without modification.

**The Electrodes.**—It was found possible in the following way to produce a spark which over a fairly wide region in its center was completely free from any lines due to the material of the electrodes. Tungsten electrodes 10–12 mm. apart were used, and these projected slightly into the flame from opposite sides. The tungsten vapor evolved is swept away by the flame gases and does not penetrate into the center of the flame. The spark was always passed just above the blue cone of the flame. Tungsten lines are apt to appear if the spark is too far above the cone. No improvement in sensitivity



was noted with closer electrodes, but tungsten lines appeared. The flame was made slightly "lean" in gas. The electrodes of the auxiliary spark were about 7 mm. apart.

**Optical Arrangement.**—A Bausch and Lomb quartz prism spectrograph was employed which has a dispersion of about 10 Å. per millimeter at  $\lambda 2800$ . The center of the spark was focused on the slit by means of a cylindric quartz lens, which was found to give a fairly uniform distribution of intensity over the entire slit.

**Sensitivity and Excitation.**—The excitation obtained under the conditions described above approximates what should be expected in a very high temperature flame. Lines of very high excitation potential which do appear in the spark are not obtained, but, on the other hand, many lines appear, especially at high concentrations, which are so weak in flames that they are not photographed under ordinary conditions. For example, Mg  $\lambda 2795$ , Mg  $\lambda 2802$ , and B  $\lambda 2479$  appear strongly, and fourteen lines of Na, Mg, Zn, Au, Cd and Tl have been identified which did not appear in the flame in comparison experiments and are absent in the acetylene flame spectrograms of Lundegårdh.<sup>2</sup> The water and cyanogen bonds, of course, occur in the spectra obtained but on the whole the plates are cleaner and freer of background than those printed by Lundegårdh.

**Photometry.**—Since the purpose of the work outlined was to compare quantitatively the intensities of pairs of lines in the spark under various conditions, it was necessary to develop a method of rapid photometry. The intensities of two light sources are ordinarily compared photographically by cutting down one or both in a known way until the images which they produce on the photographic plate have the same density. This is most conveniently done by the use of rotating sectors, which are easily constructed and require no calibration. Calibration of wedges over a range of wave lengths is very laborious and screens could not be used in the present work.

The rotating sector has been condemned by some authorities because two effects, the "failure of the reciprocity law" and the "intermittency effect" may introduce large errors, but under certain conditions of operation these are found to counteract each other to a large extent,<sup>3</sup> and within sufficient accuracy the intensities of two lines of the same density are inversely proportional to the sector opening. It is necessary that the sector speed be maintained above a certain minimum (120 r. p. m. is sufficient), that the plates used are not too "slow," and that the total exposure time be kept constant. For an intermittent source such as the electric spark, the time of a single opening of the sector should be large in comparison to the duration of the flash, and to the time between flashes.

A step sector wheel was constructed similar to that shown in Fig. 3 except that it had three times as many steps with the same total range of opening. Each opening is the cube root of two times the one below it, corresponding to a 26% increase of exposure, except for a correction which had to be made due to the fact that the cylindrical lens did not give a quite

<sup>3</sup> (a) Weinland, *J. Optical Soc. Am.*, **15**, 337 (1927); (b) Weinland, *ibid.*, **16**, 295 (1928); (c) Weber, *Ann. Physik*, **45**, 801 (1914); (d) Howe, *Phys. Rev.*, **8**, 674 (1916); (e) Newcomer, *Science*, **49**, 241 (1919); (f) Rossler, *Ber.*, **59**, 2606 (1926); (g) Gibson and co-workers, Scientific Papers of the Bureau of Standards, No. 440 (1922).

uniform illumination over the entire slit. This sector was mounted as close as possible in front of the spectrograph slit and rotated at about 120 r. p. m. Every image of a spectral line of the plate then consists of a series

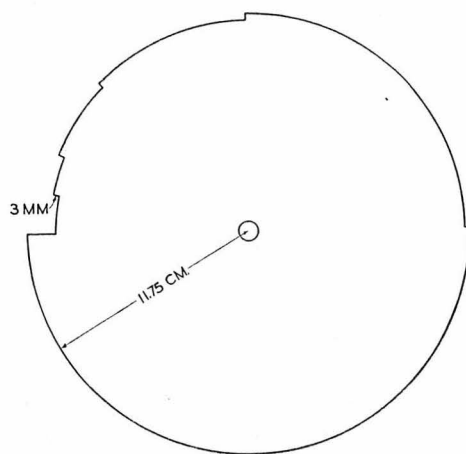


Fig. 3.—Rotating sector wheel used with photoelectric photometer.

of sections one above the other, of which the effective exposure increases logarithmically from the bottom to the top of the line.

If for a given spectral line the densities of the "sections" are plotted against the logarithms of the corresponding sector openings, a curve results whose shape depends on the characteristics of the plate and the development. Two spectral lines, sufficiently close so that the sensitivity and contrast of the plate are the same for both, will give curves of similar shape, but one will be displaced horizontally

with respect to the other by an amount equal to the logarithm of the ratio of the intensities of the two lines in the source (see Fig. 4).

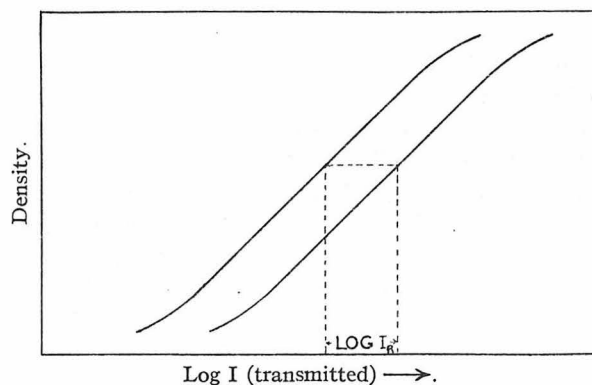


Fig. 4.—Typical intensity-photographic plate density curves for two sources of different intensities.

In practice, however, what one measures is an intensity due partly to the line emission of an element and partly to a continuous background which overlies the whole spectrum, and a correction must usually be made for the latter. It was found that where a sufficiently wide slit was used to permit of photometering the lines with an ordinary photoelectric photom-

eter, the blackening due to the background was such a large part of the total that the errors of measurement were very large.

However, it was found that the spectrograph slit could be narrowed sufficiently to make the density of the background negligible in comparison to that of the spectral lines, leaving the lines still sufficiently wide to be compared visually. When two lines were to be compared the photographic plate was cut between them, and the two portions brought into contact so that the two lines were side by side. One portion of plate was then moved up and down until opposite to one section of one line a section of the other line of equal density was found. If no exact correspondence could be found an interpolation was made. Knowing the sector openings corresponding to the sections chosen the relative intensities of the lines were easily estimated.

Two types of plates were used: Eastman D. C. Ortho with the ordinary Eastman D 61a developer, and Eastman "Regular" lantern slide plates with the contrast developer recommended. The former plates were developed for four minutes, the latter for two, stroking with a camel's hair brush, which gives exceptionally even development.

### Experimental Results and Discussion

In order to make an estimate of the accuracy which might be expected of the analysis of simple solutions using the methods outlined, some intensity-concentration curves were first determined, as shown in Fig. 5. In each case the lines of the elements studied were compared with the copper line  $\lambda 3247$ , which was photographed by making each test solution 0.01 molal in copper nitrate. These curves should not be compared too rigorously with one another, since the plate sensitivity and contrast varies somewhat over the spectral region included.

The mutual effects which various elements have on each other's excitation were then studied. Since, as mentioned above, the atomizing of reasonable amounts of substances into a suitable flame did not appreciably change its temperature or volume, two principal effects remain to be considered. The introduction of substances of low ionization potential into the flame may be expected to change the conductivity and consequently the nature of the discharge and the excitation of all other elements present. Secondly, elements of low resonance potential when added may rob other elements of high excitation potential of their energy in collisions of the second kind, and cause their emission to be diminished.

A standard solution was prepared, 0.01 molal in copper, 0.01 molal in silver, 0.1 molal in thallium and 0.1 molal in cadmium, and the spark-in-flame spectrum of this was photographed beside the spectrum of another solution which was identical except for the addition of a rather large amount (1 molal) of a fifth element. In successive experiments this added element

TABLE II

Line	Exc. v.	Percentage change in intensity due to presence of 1 molal—					Percentage error in analysis due to			
		Average	Copper	Silver	Mercury	Average	Na	Cu	Ag	Hg
3247 Cu	3.8	+26	+12	+26	+26	+23	+10	+10	+5	+5
3274 Cu	3.8	+17	+12	+20	+28	+19	+7	+7	0	-5
3281 Ag	3.7	+6	+4	+11	+14	+9	+5	+5	0	0
3384 Ag	3.6	0	0	+7	+9	+4	+5	0	+3	+3
3775 Tl	3.27	+34	+26	+26	+26	+28	-3	-2	-3	-2
3519 Tl	4.3	+51	+41	+68	+58	+54	-3	0	+11	+3
3261 Cd <sup>a</sup>	3.78	Decrease	Decrease	Decrease	Decrease	Decrease	-3	0	0	-1
3610 Cd <sup>a</sup>	7.5	Decrease	Decrease	Decrease	Decrease	Decrease	+12	+12	0	0
3460 Cd <sup>a</sup>	7.5	Decrease	Decrease	Decrease	Decrease	Decrease	0	0	+6	-5
Resonance energy of element added (volts)							-5	-5	-5	-5
Percentage error in analysis due to							+25	..	+6	0
Na							+20	..	+2	0
Cu							+18	-2	..	+6
Ag							+20	-15	..	+15
Hg							+60	+6	-4	0
Average							+90	-2	+10	-9
2.1							3.8	3.6	4.9	

<sup>a</sup> Cadmium lines were too weak to estimate accurately, but intensity change was small (less than 20%).

was varied, elements being chosen with widely different resonance and ionization potentials. The percentage changes in the intensities of certain copper, silver and thallium lines due to the addition of the "impurity" are given in Table II. The four determinations indicate the accuracy of the intensity comparisons.

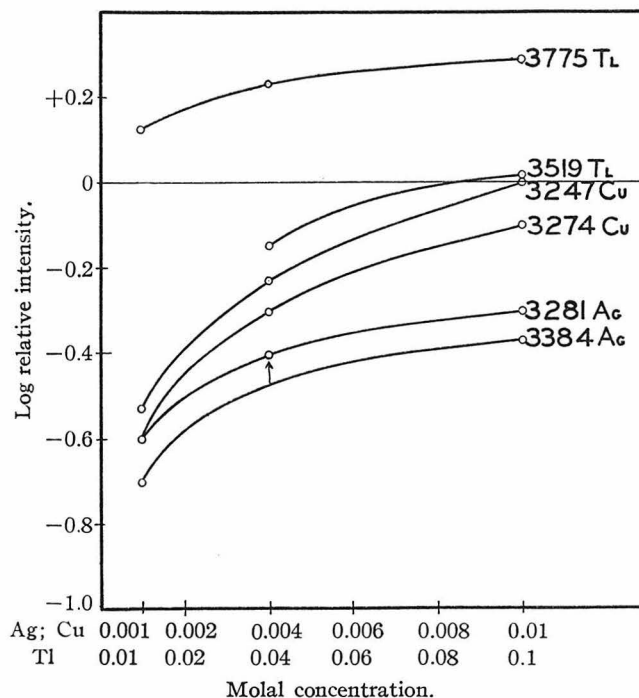


Fig. 5.—Intensity-concentration curves for several elements.

It will be noticed that the line intensities are usually increased by the "impurity" probably due to the increased conductivity of the flame gases. The last four columns of the table show the per cent. errors which these changes in intensity would cause in an analysis for copper, silver and thallium in case unknown solutions of approximately the same composition as those of the four solutions containing the "impurities" were compared directly with a test solution containing the three elements in the same concentration, but without the impurity. It will be seen that these errors are not larger than the average error of estimation except in the case of sodium.

### Conclusion

One of the principal objects of the present work was to find conditions under which the spectroscopic analysis of solutions containing several elements in rather widely varying relative concentrations can be made rapidly

without elaborate calibration experiments being necessary for each special case. Since under the conditions of the spark-in-flame the mutual effects of elements are in general not large, it appears that such analyses can be carried out with moderate precision if the intensities of the lines emitted by the unknown solutions are compared directly with the concentration intensity curves which have been determined once and for all on pure test solutions of the elements in which one is interested. In case alkali metals are present in high concentration their effect can be to a considerable extent allowed for by the addition, in known concentration, of a reference element absent in the unknown. This is the method of "Leitlinien" discussed by Lundegårdh.<sup>2</sup>

#### Summary

1. A new method of exciting spectra for the purpose of quantitative chemical analysis has been developed and studied. It consists in passing a condensed spark discharge through a flame into which is atomized a solution of the sample to be analyzed.
2. The excitation obtained, though less than that of the ordinary spark, is similar to that which should be expected in a flame of very high temperature, and many lines appear which are absent in ordinary flame spectra.
3. The mutual effects of some elements on each other's emission in the spark-in-flame have been studied, and these have been found small enough to permit of a semi-quantitative analysis of unknown solutions containing several elements, without elaborate calibration experiments.

PASADENA, CALIFORNIA

## Equivalent Chemical Bonds Formed by *s*, *p*, and *d* Eigenfunctions\*

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1. The work of Pauling on the linear combinations of eigenfunctions to form bond functions has been extended.
2. A theorem concerning the maximum strength in a given direction of a bond function orthogonal to existing bond functions has been derived. It is found that the strongest bond functions must lie at such angles to one another that the maximum of each coincides with a node of each of the others.
3. A general expression for equivalent Pauling bond functions formed from linear combinations of *s*, *p*, and *d* eigenfunctions has been derived.
4. By assuming the bond functions to have cylindrical symmetry, like the best possible bond functions, the equations can be readily solved. It is found that equivalent cylindrical bond functions will be orthogonal if the angles between every pair have no more than two values. The angles must be greater than  $54^{\circ}44'$  and their sum must be greater than  $180^{\circ}$ ; otherwise they are unrestricted. No more than six such bond functions may be formed. Solutions for six and less equivalent bond functions are given.
5. There are only four possible configurations for six equivalent cylindrical bond functions. Two of these are much weaker than the other two and so are improbable. The configurations for the stronger bond functions are in striking agreement with the only two structures, the octahedron and the trigonal prism, which are found experimentally.
6. A discussion of the factors influencing bond energies is made and examples of chemical compounds cited. It is predicted that the structure of  $P_4$  is that of a tetrahedron with a *P* atom at each corner.

### I. INTRODUCTION

IN THE theory of directed bonds of Pauling and Slater the bonds formed by a given atom tend to assume certain directions relative to one another; namely, those in which the single electron eigenfunctions of the atom have their maximum concentration, permitting maximum "overlapping" with the eigenfunctions of the other atoms with which bonds are formed. The prediction of bond angles is reduced by this theory to the determination of these directions; moreover, some information regarding the strength of a bond can be obtained from the consideration of the amount of concentration of the bond eigenfunction in the bond direction.

In the simple approximate treatment given by Pauling,<sup>1</sup> it is assumed that the bond eigenfunctions are formed by linear combination of a set of eigenfunctions

$$\Psi_{nlm}(r, \theta, \phi) = R_{nl}(r)P_l^{lm}(\cos \theta) \{A \cos m\phi + B \sin m\phi\}$$

( $P_l^m(\cos \theta)$  is Ferrer's associated Legendre polynomial)

\* (Contribution from Gates Chemical Laboratory, California Institute of Technology, No. 317.)

<sup>1</sup> Linus Pauling, J. Am. Chem. Soc. **53**, 1367 (1931).

which have approximately the same energy. The coefficients in the linear combinations are determined by a consideration of the  $\theta, \phi$  parts of the functions only, it being assumed that the  $r$  parts are similar (though not identical) in all of the functions. Neglecting the  $r$  part, the eigenfunctions with  $l=0, 1$ , and  $2$ ,  $\dots$  normalized to  $4\pi$ , are:

$$\begin{array}{lll} s & = P_0^0(\cos \theta) & = 1 \\ p_z & = (3)^{1/2} P_1^0(\cos \theta) & = (3)^{1/2} \cos \theta \\ p_x & = (3)^{1/2} P_1^1(\cos \theta) \cos \phi & = (3)^{1/2} \sin \theta \cos \phi \\ p_y & = (3)^{1/2} P_1^1(\cos \theta) \sin \phi & = (3)^{1/2} \sin \theta \sin \phi \\ d_z & = (5)^{1/2} P_2^0(\cos \theta) & = \frac{1}{2}(5)^{1/2}(3 \cos^2 \theta - 1) \\ d_{x+z} & = [(15)^{1/2}/3] P_2^1(\cos \theta) \cos \phi & = (15)^{1/2} \sin \theta \cos \theta \cos \phi \\ d_{y+z} & = [(15)^{1/2}/3] P_2^1(\cos \theta) \sin \phi & = (15)^{1/2} \sin \theta \cos \theta \sin \phi \\ d_x & = [(15)^{1/2}/12] P_2^2(\cos \theta) \cos 2\phi & = \frac{1}{2}(15)^{1/2} \sin^2 \theta \cos 2\phi \\ d_{x+y} & = [(15)^{1/2}/12] P_2^2(\cos \theta) \sin 2\phi & = \frac{1}{2}(15)^{1/2} \sin^2 \theta \sin 2\phi \end{array}$$

The maximum values of these eigenfunctions are 1.000 for  $s$ , 1.732 for  $p_x, p_y$ , and  $p_z$ , 2.236 for  $d_z$ , and 1.936 for the other  $d$  eigenfunctions. For polar graphs of these see reference 1. (More bond functions of the same shape and strength as the  $d_z$  function can be formed by linear combinations of the other  $d$  functions.) These values are called the "strengths" of the bond functions, inasmuch as they indicate the amount of concentration of the functions in particular directions and hence give a rough measure of the bond-forming power of the functions. The meaning of the *strength* in terms of energy units has not been determined, but the resonance energy undoubtedly increases rapidly with the strength.

In certain cases, as in  $C(1s^2 2s 2p 2p 2p)$ , the  $s$ - $p$  quantization may be broken and stronger bond functions can then be formed using linear combinations of  $s$  and  $p$  eigenfunctions. The strongest possible  $s$ - $p$  bond functions have a strength of 2.000 and are directed to the four corners of a tetrahedron, in agreement with the tetrahedral carbon atom long known to organic chemists and accounting for many other bond angles of about  $109^\circ 28'$ .<sup>1</sup>

For elements of the long periods, the  $d$  eigenfunctions probably play an important part in bond formation, since, for example, the  $3d$  term value for elements of the first long period has probably not a greatly different energy from that of the  $4s$  level. Just as in the case of  $s$  and  $p$  eigenfunctions the quantization may be broken and  $s$ - $p$ - $d$ ,  $s$ - $d$ , or  $p$ - $d$  combinations may be formed.

In this paper a method for finding the best equivalent  $s$ - $p$ - $d$  bond functions will be developed. The equations prove to be too complex to be solved in the general case, but by making the reasonable assumption that the bond functions have cylindrical symmetry (the best possible bond functions do have cylindrical symmetry), solutions are obtained which cannot be far from the best.

## II. THE MAXIMUM STRENGTH OF BOND FUNCTIONS

It has been shown by Pauling (reference 1) that the strongest bond function  $\Psi_j = \sum_{k=1}^m a_{jk} \psi_k(\theta, \phi)$  which can be formed in the direction  $\theta_0, \phi_0$  has a



strength in that direction  $\Psi_j(\theta_0, \phi_0) = \{\sum_{k=1}^m [\psi_k(\theta_0, \phi_0)]^2\}^{1/2}$ . If it be required that this bond function be orthogonal to  $n$  pre-existing bond functions  $\Psi_i(\theta, \phi) = \sum_{k=1}^m a_{ik} \psi_k(\theta, \phi)$ , it can be shown (See appendix I) that the maximum strength is reduced to

$$\Psi_j(\theta_0, \phi_0) = \left\{ \sum_{k=1}^m [\psi_k(\theta_0, \phi_0)]^2 - \sum_{i=1}^n [\Psi_i(\theta_0, \phi_0)]^2 \right\}^{1/2}.$$

When the range of summation  $m$  comprises only completed subgroups, the first term is equal to  $m$ , and the formula becomes

$$\Psi_j(\theta_0, \phi_0) = \left\{ m - \sum_{i=1}^n [\Psi_i(\theta_0, \phi_0)]^2 \right\}^{1/2}.$$

If some of the eigenfunctions of the subgroups are excluded from bond formation, as is the case when they are occupied by an unshared pair of electrons, the formula still holds, providing these excluded eigenfunctions are treated as pre-existing bond functions.

This theorem gives us several important conclusions at once. *The strongest bond functions lie at such angles to one another that the maximum of each coincides with a node of each of the others.* In general, only three such bond functions are geometrically possible. For  $s$ - $p$  bond functions, however, as we have seen, the nodal angle of  $109^\circ 28'$  allows the construction of four.

The best  $s$ - $p$ - $d$  bond function (reference 1) (with the maximum along the  $z$  axis) is

$$\Psi = \frac{1}{3}s + \frac{1}{(3)^{1/2}}p_z + \frac{(5)^{1/2}}{3}d_z.$$

It has a strength of  $(9)^{1/2}$  and has nodes at  $73^\circ 09'$  and  $133^\circ 37'$ . We may conclude that  *$s$ - $p$ - $d$  bonds tend to form at angles of  $73^\circ 09'$  and  $133^\circ 37'$ . The closer the bond angles approach these values, the greater will be the resonance energy of the bond.* Only three of these bonds are geometrically possible and, as will be shown later, these angles may be modified considerably in the case of larger coordination numbers by orthogonality conditions.

In the same way it may be seen that the best  $p$  bond functions have a strength of  $(3)^{1/2}$  and are formed at angles of  $90^\circ$ ; the best  $d$  bond functions have a strength of  $(5)^{1/2}$  and angles  $54^\circ 44'$  and  $125^\circ 16'$ ; the best  $p$ - $d$  bond functions have a strength  $(8)^{1/2}$  and angles  $65^\circ 44'$  and  $144^\circ 12'$ ; and the best  $s$ - $d$  bond functions have a strength  $(6)^{1/2}$  and angles  $63^\circ 26'$  and  $116^\circ 34'$ .

### III. EQUIVALENT BOND FUNCTIONS

Two bond functions may be defined as equivalent when they differ from one another by a rotation only. A method of finding equivalent bonds is to set up the most general  $s$ - $p$ - $d$  eigenfunction containing shape parameters and orientation parameters. Two eigenfunctions with the same values of the shape parameters will be equivalent.

Denoting the generalized eigenfunctions by capital letters, we have:

$$P = ap_z + bp_x + cp_y = \frac{(3)^{1/2}}{r}(ax + by + cz).$$

But by a rotation transformation  $P$  can be expressed as  $a'z'/r$ , with  $z'$  measured along an axis with direction cosines  $a:b:c$ . Hence  $a$ ,  $b$ , and  $c$  are orientation and not shape parameters, and the most general shape of  $P$  is  $P = p_z$ . It may also be shown (See appendix II) that the most general  $D$  eigenfunction has the shape of a linear combination of  $d_z$  and  $d_x$ .

We can now express the most general  $s$ - $p$ - $d$  bond function as a linear combination of arbitrarily oriented  $S$ ,  $P$ , and  $D$  eigenfunctions. The most general shape of the function, that is, the shape of the polar graph of strength against direction, will be determined by five parameters; three of them determine the relative amounts of  $s$ ,  $p_z$ ,  $d_z$ , and  $d_x$  which are in the bond (there are not four because of the normalization condition), and two the relative orientation of  $P$  to  $D$ . The orientation parameters may be determined by carrying out a rotation transformation on these eigenfunctions. This may be most conveniently done by rotating the axes as follows: Rotate through an angle  $\phi_d'$  about the  $z$  axis, then through  $\theta_d$  about the  $y$  axis, then through  $\phi_d$  about the  $z$  axis. The behavior of our functions under these transformations is discussed in appendix III, in which the following expression for an  $s$ - $p$ - $d$  bond function of arbitrary shape and orientation is obtained:

$$\begin{aligned} \Psi = & \sin \alpha \sin \beta s + \sin \alpha \cos \beta \{ [\cos \theta_p \cos \theta_d - \sin \theta_p \sin \theta_d \cos (\phi_p + \phi_d')] p_z \\ & + [\cos \theta_p \sin \theta_d \cos \phi_d + \sin \theta_p \cos \theta_d \cos (\phi_p + \phi_d') \cos \phi_d \\ & - \sin \theta_p \sin (\phi_p + \phi_d') \sin \phi_d] p_x + [\cos \theta_p \sin \theta_d \sin \phi_d \\ & + \sin \theta_p \cos \theta_d \cos (\phi_p + \phi_d') \sin \phi_d + \sin \theta_p \sin (\phi_p + \phi_d') \cos \phi_d] p_y \} \\ & + \cos \alpha \{ [(3/2) \cos \gamma \cos^2 \theta_d - \frac{1}{2} \cos \gamma + \frac{1}{2}(3)^{1/2} \sin \gamma \sin^2 \theta_d \cos 2\phi_d'] d_z \\ & + [\frac{1}{2}(3)^{1/2} \cos \gamma \sin^2 \theta_d \cos 2\phi_d + \sin \gamma \cos 2\phi_d \cos 2\phi_d'] \\ & - \frac{1}{2} \sin \gamma \sin^2 \theta_d \cos 2\phi_d \cos 2\phi_d' - \sin \gamma \cos \theta_d \sin 2\phi_d \sin 2\phi_d'] d_x \\ & + [\frac{1}{2}(3)^{1/2} \cos \gamma \sin^2 \theta_d \sin 2\phi_d + \sin \gamma \sin 2\phi_d \cos 2\phi_d' \\ & - \frac{1}{2} \sin \gamma \sin^2 \theta_d \sin 2\phi_d \cos 2\phi_d' + \sin \gamma \cos \theta_d \cos 2\phi_d \sin 2\phi_d'] d_{x+y} \\ & + [\frac{1}{2}(3)^{1/2} \cos \gamma \sin 2\theta_d \cos \phi_d + \sin \gamma \sin \theta_d \sin \phi_d \sin 2\phi_d' \\ & - \frac{1}{2} \sin \gamma \sin 2\theta_d \cos \phi_d \cos 2\phi_d'] d_{x+z} + [\frac{1}{2}(3)^{1/2} \cos \gamma \sin 2\theta_d \sin \phi_d \\ & - \sin \gamma \sin \theta_d \cos \phi_d \sin 2\phi_d' - \frac{1}{2} \sin \gamma \sin 2\theta_d \sin \phi_d \cos 2\phi_d'] d_{y+z}. \end{aligned}$$

$\alpha$ ,  $\beta$  = shape parameters determining relative amounts of  $S$ ,  $P$ , and  $D$  used;  $\gamma$  = shape parameter determining relative amounts of  $d_z$  and  $d_x$  used;  $\theta_p$ ,  $\phi_p$  = shape parameters determining relative orientation of  $P$  to  $D$ ;  $\theta_d$ ,  $\phi_d$  = direction of  $z$  axis after rotation;  $\phi_d'$  = rotation of bond function about new  $z$  axis.

The eigenfunction is normalized as written and the only restrictions on the values of the coefficients are the orthogonality conditions. For  $n$  bond functions these give  $\frac{1}{2}n(n-1)$  equations containing 5 shape parameters and  $3n-3$  arbitrary orientation parameters (three may be arbitrarily chosen without loss of generality). The equations are not necessarily independent. If the number of independent equations exceeds the number of unknowns, they are said to be over-determined, and there is no solution. If the numbers are equal, there will be one or more single points in the hyper space which satisfy the equation; while if the number of equations is less, there will be sets of continuous solutions. For certain values of some of the parameters the number of independent equations may be reduced.

From other considerations it seems probable that nine equivalent bond functions (36 equations, 29 unknowns) cannot be formed. The existence of solutions for eight bond functions, having 28 equations and 26 unknowns, is doubtful; but for seven or less bond functions there probably should be continuous solutions.

Unfortunately the orthogonality equations are extremely complicated, each equation containing 46 terms and involving 11 parameters. But by making certain reasonable approximations, we can reduce the equations to a readily soluble form. The best possible  $s$ - $p$ - $d$  bond function is symmetrical about the direction where it has its maximum value and has the following values of the shape parameters:

$$\begin{aligned}\theta_p &= 0 \text{ (then } \phi_p \text{ may be arbitrary),} & \alpha &= \cos^{-1} (5)^{1/2}/3, \\ \gamma &= 0, & \beta &= \cos^{-1} \frac{1}{2}(3)^{1/2}.\end{aligned}$$

An increase in  $\gamma$  will quickly reduce the possible bond strength by scattering the  $d$  eigenfunction, so any really strong bond function must have  $\gamma$  nearly equal to zero. We may therefore set  $\gamma = 0$  with a feeling of considerable confidence that this arbitrary restriction has not eliminated any important bond eigenfunctions which are not rather closely approximated by one of those remaining. The same argument applies to  $\theta_p$  except that the decrease in strength is not rapid. We shall assume that the  $p$  part of the bond function has its maximum in the same direction as the  $d$  part ( $\theta_p = 0$ ).

These assumptions enormously simplify the orthogonality equations; the number of terms is reduced from 46 to 9 and the number of parameters from 11 to 6. Furthermore the direction of the maximum value of the bond functions is easy to find; it is  $\theta$ ,  $\phi = \theta_d$ ,  $\phi_d$ . These are the only  $s$ - $p$ - $d$  combinations with cylindrical symmetry, and will be referred to as *cylindrical bond functions*.

#### IV. CYLINDRICAL BOND FUNCTIONS

The above treatment gives us the following expression for the general cylindrical bond function

$$\begin{aligned}\Psi &= \sin \alpha \sin \beta s + \sin \alpha \cos \beta [\cos \theta_d p_z + \sin \theta_d \cos \phi_d p_x + \sin \theta_d \sin \phi_d p_y] \\ &+ \frac{1}{2} \cos \alpha [(3 \cos^2 \theta_d - 1) d_z + (3)^{1/2} \sin^2 \theta_d \cos 2\phi_d d_x + (3)^{1/2} \sin^2 \theta_d \sin 2\phi_d d_{x+y} \\ &+ (3)^{1/2} \sin 2\theta_d \cos \phi_d d_{x+z} + (3)^{1/2} \sin 2\theta_d \sin \phi_d d_{y+z}].\end{aligned}$$

If we place one bond function with its maximum along the  $z$  axis, all bond functions orthogonal to it must obey the equation:

$$\sin^2 \alpha \sin^2 \beta + \sin^2 \alpha \cos^2 \beta \cos \theta_d + \frac{1}{2} \cos^2 \alpha (3 \cos^2 \theta_d - 1) = 0.$$

This is a quadratic in  $\cos \theta_d$  and so has two solutions in terms of  $\alpha$  and  $\beta$ . Hence the equivalent cylindrical bond functions orthogonal to a function of a given shape must have the loci of their maxima in two cones, which are determined by the shape parameters. Conversely, any two angles will determine the shape parameters.

$$\sin \alpha = \left( \frac{(1 - \cos \theta)(1 - \cos \theta') - \frac{2}{3}}{(1 - \cos \theta)(1 - \cos \theta')} \right)^{1/2}$$

$$\sin \beta = \left( \frac{\cos \theta \cos \theta' + \frac{1}{3}}{(1 - \cos \theta)(1 - \cos \theta') - \frac{2}{3}} \right)^{1/2}.$$

In order to have real solutions, the angles must be restricted as follows:

$$\theta, \theta' \geq 54^\circ 44' \quad \theta + \theta' \geq 180^\circ.$$

Then all bond functions having their maxima at angles  $\theta$  or  $\theta'$  to the maximum of the given bond function will be orthogonal to it, providing the shape parameters are chosen correctly. This can easily be extended by symmetry to include all bond functions of the set, giving the general theorem: *The necessary and sufficient condition for a set of equivalent s-p-d cylindrical bond functions to be orthogonal is that there be no more than two different values for the angles between the direction of the maximum of any given bond function and the direction of the maxima of all the other bond functions.* The shape parameters must be chosen and the angles restricted as given above.

This theorem reduces our problem to the purely geometrical one of finding the ways that  $n$  vectors may be oriented such that the angles between all pairs obey the above restriction. It can be easily shown that no more than six vectors may be so placed: *No more than six equivalent cylindrical bond functions can be orthogonal to one another.*

For any values of the angles which satisfy the orthogonality conditions, the strength will be found to be

$$\text{Strength} = \frac{(\cos \theta \cos \theta' + \frac{1}{3})^{1/2} + (-3(\cos \theta + \cos \theta'))^{1/2} + (10/3)^{1/2}}{((1 - \cos \theta)(1 - \cos \theta'))^{1/2}}.$$

### Six equivalent cylindrical bond functions

If we place one vector along the  $z$  axis, there may be as many as five in the  $\theta$  cone, if they are evenly spaced; that is,  $\Delta\phi = 72^\circ$  or  $144^\circ$ . If we now make the angles between the vectors equal to  $\theta$  or  $\theta'$  by use of the distance formula of spherical trigonometry:  $\cos \delta = \cos \theta_1 \cos \theta_2 + \sin \theta_1 \sin \theta_2 \cos(\phi_1 - \phi_2)$  where in this case  $\delta = \theta$  or  $\theta'$ ;  $\theta_1$  and  $\theta_2 = \theta$ ; and  $\phi_1 - \phi_2 = 72^\circ$  or  $144^\circ$ , we get two similar solutions. Placing four bonds in the  $\theta$  cone and one in the  $\theta'$  gives us another solution, the octahedral configuration discovered by Pauling.<sup>1</sup> There

is only one more solution; in which the vectors point to the corners of an equilateral triangular prism with square sides.

The first two solutions contain no  $p$  eigenfunctions. They are the strongest  $s$ - $d$  bond functions that can be formed.

The six equivalent octahedral eigenfunctions<sup>1</sup> are:

$$\begin{aligned}\Psi_1 &= \frac{1}{6^{1/2}} s + \frac{1}{2^{1/2}} p_z + \frac{1}{3^{1/2}} d_z, \\ \Psi_2 &= \frac{1}{6^{1/2}} s - \frac{1}{2^{1/2}} p_z + \frac{1}{3^{1/2}} d_z, \\ \Psi_3 &= \frac{1}{6^{1/2}} s + \frac{1}{2^{1/2}} p_x - \frac{1}{12^{1/2}} d_z + \frac{1}{2} d_x, \\ \Psi_4 &= \frac{1}{6^{1/2}} s - \frac{1}{2^{1/2}} p_x - \frac{1}{12^{1/2}} d_z + \frac{1}{2} d_x, \\ \Psi_5 &= \frac{1}{6^{1/2}} s + \frac{1}{2^{1/2}} p_y - \frac{1}{12^{1/2}} d_z - \frac{1}{2} d_x, \\ \Psi_6 &= \frac{1}{6^{1/2}} s - \frac{1}{2^{1/2}} p_y - \frac{1}{12^{1/2}} d_z - \frac{1}{2} d_x,\end{aligned}$$

with three pure  $d$  eigenfunctions orthogonal to them

$$\Psi_7 = d_{x+y}; \Psi_8 = d_{x+z}; \Psi_9 = d_{y+z}.$$

The trigonal prism eigenfunctions are:

$$\begin{aligned}\Psi_1 &= \frac{51^{1/2}}{18} s + \frac{1}{6^{1/2}} p_z + \frac{1}{3} 2^{1/2} p_x + \frac{1}{6(3)^{1/2}} d_z + \frac{1}{3} d_x \\ &\quad + \frac{1}{3^{1/2}} d_{x+z} \\ \Psi_2 &= \frac{51^{1/2}}{18} s + \frac{1}{6^{1/2}} p_z - \frac{1}{6} 2^{1/2} p_x + \frac{1}{6^{1/2}} p_y + \frac{1}{6(3)^{1/2}} d_z - \frac{1}{6} d_x \\ &\quad - \frac{1}{2(3)^{1/2}} d_{x+y} - \frac{1}{2(3)^{1/2}} d_{x+z} + \frac{1}{2} d_{y+z} \\ \Psi_3 &= \frac{51^{1/2}}{18} s + \frac{1}{6^{1/2}} p_z - \frac{1}{6} 2^{1/2} p_x - \frac{1}{6^{1/2}} p_y + \frac{1}{6(3)^{1/2}} d_z - \frac{1}{6} d_x \\ &\quad + \frac{1}{2(3)^{1/2}} d_{x+y} - \frac{1}{2(3)^{1/2}} d_{x+z} - \frac{1}{2} d_{y+z} \\ \Psi_4 &= \frac{51^{1/2}}{18} s - \frac{1}{6^{1/2}} p_z + \frac{1}{3} 2^{1/2} p_x + \frac{1}{6(3)^{1/2}} d_z + \frac{1}{3} d_x \\ &\quad - \frac{1}{(3)^{1/2}} d_{x+z}\end{aligned}$$

$$\begin{aligned}\Psi_5 &= \frac{51^{1/2}}{18} s - \frac{1}{6^{1/2}} p_z - \frac{1}{6} 2^{1/2} p_x + \frac{1}{6^{1/2}} p_y + \frac{1}{6(3)^{1/2}} d_z - \frac{1}{6} d_x \\ &\quad - \frac{1}{2(3)^{1/2}} d_{x+y} + \frac{1}{2(3)^{1/2}} d_{x+z} - \frac{1}{2} d_{y+z} \\ \Psi_6 &= \frac{51^{1/2}}{18} s - \frac{1}{6^{1/2}} p_z - \frac{1}{6} 2^{1/2} p_x - \frac{1}{6^{1/2}} p_y + \frac{1}{6(3)^{1/2}} d_z - \frac{1}{6} d_x \\ &\quad + \frac{1}{2(3)^{1/2}} d_{x+y} + \frac{1}{2(3)^{1/2}} d_{x+z} + \frac{1}{2} d_{y+z}\end{aligned}$$

with the following eigenfunctions remaining.

$$\Psi_7 = \frac{1}{18^{1/2}} s - \frac{17^{1/2}}{18^{1/2}} d_z; \quad \Psi_8 = \frac{1}{3^{1/2}} p_x - \frac{2^{1/2}}{3^{1/2}} d_x; \quad \Psi_9 = \frac{1}{3^{1/2}} p_y + \frac{2^{1/2}}{3^{1/2}} d_{x+y}.$$

### Five equivalent cylindrical bond functions

Solutions may of course be obtained by leaving out one bond function of our six-bond solutions. There is also a solution obtained by placing four bond

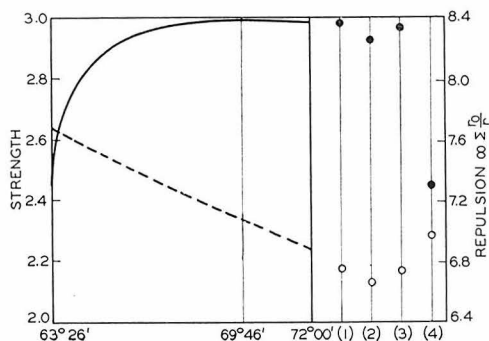


Fig. 1. Strengths of five equivalent cylindrical bonds for all possible configurations. The dotted curve represents a quantity proportional to the energy of possible electrostatic repulsion between the atoms surrounding the central atom. The configuration of maximum strength and minimum repulsion is favored. (1)  $\theta = 81^\circ 47'$ ;  $\theta' = 135^\circ 35'$ , (2)  $\theta = 90^\circ$ ;  $\theta' = 180^\circ$  (3)  $\theta = 120^\circ$ ;  $\theta' = 75^\circ 31'$  (4)  $\theta = 63^\circ 26'$ ;  $\theta' = 116^\circ 34'$ .

functions equally spaced in a cone  $120^\circ$  from the fifth bond function. These bond functions have a strength of 2.968, with  $\theta' = 75^\circ 31'$ . The conditions are also satisfied by the following relation between  $\theta$  and  $\theta'$ .

$$\cos \theta' = \frac{1}{2}(3 \pm (5)^{1/2}) \cos \theta - \frac{1}{2}(1 \pm (5)^{1/2}).$$

In these solutions the five bonds are equally spaced in a cone. The strengths are shown as a function of the angle  $\theta$  in Fig. 1, the maximum strength being 2.994. The energies of steric repulsion are qualitatively indicated by the dotted line.

#### Four equivalent cylindrical bond functions

In this case there are six sets of continuous solutions, which include all the previously given solutions for a greater number of bond functions.

$$\cos \theta' = \frac{1}{2}(3 \cos^2 \theta - 1) \quad (1)$$

$$\cos \theta' = \frac{4 \cos^2 \theta}{1 + \cos \theta} - 1 \quad (2)$$

$$\cos \theta' = \cos^2 \theta \pm (1 - \cos \theta)(\cos^2 \theta + (3/2) \cos \theta + \frac{1}{2})^{1/2} \quad (3)$$

$$\cos \theta' = \pm 2 \cos \theta - 1 \quad (4)$$

$$\cos \theta' = \frac{1}{2}(3 \cos \theta - 1 + (5)^{1/2}(\cos \theta - 1)) \quad (5)$$

$$\cos \theta' = \frac{1}{2}[1 - \cos \theta - (5 + 2 \cos \theta - 3 \cos^2 \theta)^{1/2}] \quad (6)$$

The strengths of bond functions for these solutions are shown in Fig. 2. The strongest bond function is obtained from solution (a). It has angles of  $136^\circ 06'$  and  $73^\circ 49'$  and a strength of 2.9992. Single points on two of the curves represent bond functions which contain no  $s$ , that is, they represent  $p$ - $d$  bond functions. These are at the largest angles of solutions (a) and (d). The strengths here are respectively 2.828 and 2.817, only slightly weaker than the best  $p$ - $d$  bond function, which has a strength of 2.8284.

#### V. DISCUSSION AND APPLICATION OF RESULTS

The configuration assumed by an actual molecule is not, of course, determined solely by the resonance energy but, rather, by the position of minimum potential energy. If the bond is to a considerable extent ionic in character, the resonance energy may become unimportant. In any case forces between the atoms surrounding the central atom, if they are large, will be expected to deform the bond angles from the positions where the bond functions are a maximum. These forces<sup>2</sup> may result from interaction between the dipoles of the bonds (electrostatic forces), from interaction between dipole and bond by induction, or by steric hindrance when atoms or groups are close together. For equivalent bonds, these forces will always tend to make the bond angle larger. The bond energy will also be influenced by the term values of the eigenfunctions used in the bond function and by the term values of the non-bonding electrons. If we neglect the energy of the perturbation caused by bond formation, that set of bond functions will be favored which allows the maximum number of electrons to occupy eigenfunctions of low term values. The energy of eigenfunctions occupied by unshared electron pairs will be more important than the energy of a bond eigenfunction because two electrons are involved compared with one in the bond. Unshared pairs are apt to occupy the eigenfunctions of lowest energy, so that these eigenfunctions cannot be used in the construction of bond functions.

<sup>2</sup> H. A. Stuart, Phys. Rev. **38**, 1372 (1931).

## Six equivalent bonds

The first two solutions in Table I have an advantage only in case the  $p$  levels lie considerably lower than the others, in which case unshared pairs might occupy them and exclude them from bond formation; or if the  $p$  levels

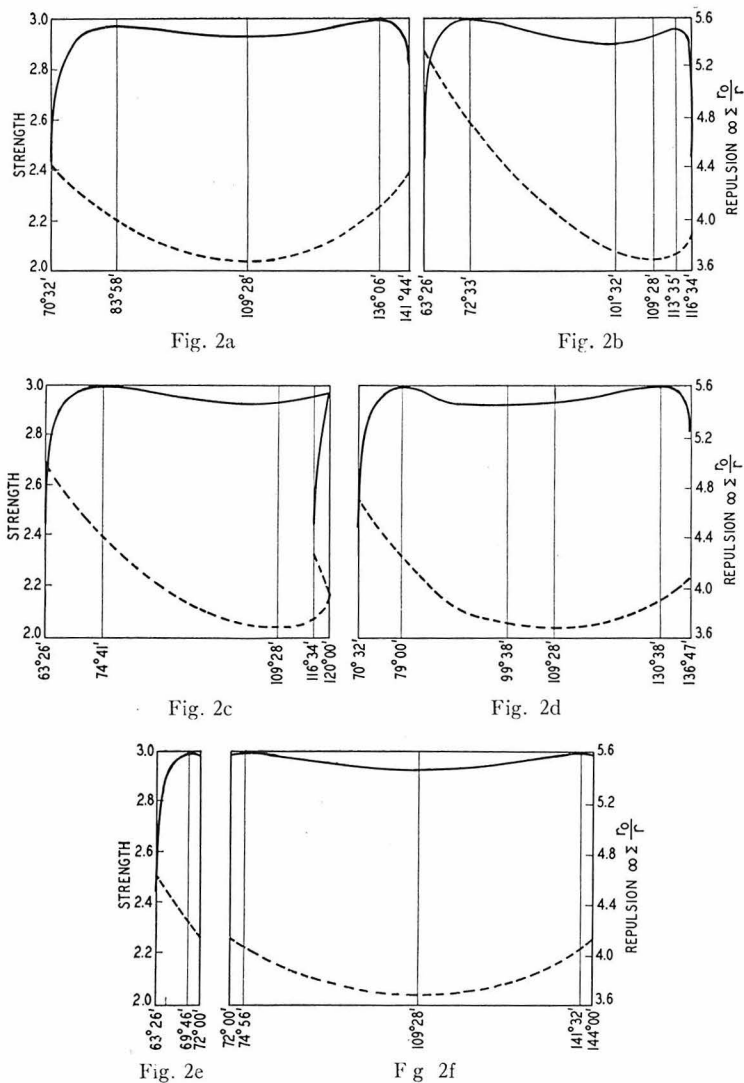


Fig. 2. Strengths and possible electrostatic repulsions of four equivalent cylindrical bonds.

lie considerably higher (with no unshared electron pairs present) so that it would be advantageous not to include them in the bond. There do not seem to be any atoms with large enough separations of energies to compensate for the much weaker bond functions of these solutions.

This leaves for consideration only two configurations, the octahedron and the trigonal prism. As a matter of fact, these are the only two structures



known experimentally, the former being found in the great majority of cases. The trigonal prism is found in molybdenite,  $\text{MoS}_2$ , and in tungstenite,  $\text{WS}_2$ . The quantitative experimental data for molybdenite<sup>3</sup> are in striking agreement with the theoretical structure. Each Mo atom is at the center of a trigonal prism whose six corners are occupied by sulfur atoms, the ratio of altitude to base of this regular triangular prism being  $1.007 \pm 0.039$  compared to the theoretical ratio of 1.000.

TABLE I. *Sets of six equivalent cylindrical bond functions.*

	Angles between bonds		No. of angles		Bond strength	Remarks
	$\theta$	$\theta'$	$\theta$	$\theta'$		
(1)	63°26'	116°34'	10	5	2.449	Five bonds in cone. <i>s-d</i> bond fns.
(2)	116°34'	63°26'	10	5	2.449	Five bonds in cone. <i>s-d</i> bond fns.
(3)	90°00'	180°00'	12	3	2.924	Octahedral bonds
(4)	81°47'	135°35'	9	6	2.983	Trigonal prism bonds

The trigonal prism configuration has greater resonance energy per bond, but the octahedron has smaller repulsive forces between the surrounding atoms. The octahedron will be preferred for bonds which are appreciably ionic in character, or for large atoms surrounding the nuclear atom. Since it contains a smaller amount of *d*, it will also be favored where the *d* level lies highest, as in elements of the second period. Where the *d* level lies lowest, the trigonal prism will be favored, unless there are unshared electron pairs. One such pair can be accommodated in the second  $\Psi_7$  eigenfunction given on page 898 which contains 17/18 *d*. But the second pair will have to be excited up to the  $\Psi_8$  level. The fact that molybdenite is diamagnetic<sup>4</sup> indicates that in molybdenum this level is higher than  $\Psi_7$  by an amount greater than the singlet-triplet separation. Hence, where the *d* level lies lowest, two or three unshared electron pairs strongly favor the octahedron, in which the pairs may all be placed in *d* levels.

#### Five equivalent bonds

The continuous solution gives a slight increase in resonance energy over the trigonal prism solution with one bond left out, but is considerably poorer sterically. The other new solution is poorer than the trigonal prism with one bond missing, both sterically and in bond strength.  $\text{PCl}_5$ , the structure of which is unknown, would be expected to have *s-p-d* bonds. It is difficult to estimate the magnitude of steric forces, but they are certainly much larger in  $\text{PCl}_5$  than in molybdenite. Probably the octahedral configuration with one bond missing (square pyramid) of some sterically more favorable configuration involving non-cylindrical bonds is assumed by this molecule.

#### Four equivalent bonds

Neglecting a few exceptional regions, where other solutions give slightly better results, the solution shown in Fig. 2a is best both sterically and in bond

<sup>3</sup> Roscoe G. Dickinson and Linus Pauling, J. Am. Chem. Soc. **45**, 1466 (1923).

<sup>4</sup> E. B. Wilson, Jr., private communication.

strength. Bonds of this type will then lie at the configuration for maximum resonance energy, or will be deformed toward the tetrahedral configuration, the most favored sterically, along the curve given. If only one  $d$  eigenfunction is available, the best bonds are directed to the corners of a square, as shown by Pauling.<sup>1</sup>

As previously mentioned, *three equivalent bonds* of the maximum strength, 3.000, may be formed at angles of  $73^\circ 09'$  and  $133^\circ 37'$ . For the configuration most favored sterically, three bonds in a plane at  $120^\circ$ , the strength is 2.881.

*Two bonds* of strength 3.000 at  $133^\circ 37'$  may be deformed to  $180^\circ$ , reducing the strength slightly to 2.96. This latter configuration will be expected when only one  $d$  eigenfunction is available. The functions are

$$\Psi_1 = (1/12^{1/2})s + (1/2^{1/2})p_z + (5^{1/2}/12^{1/2})d_z$$

$$\Psi_2 = (1/12^{1/2})s - (1/2^{1/2})p_z + (5^{1/2}/12^{1/2})d_z$$

with the unshared pair of electrons occupying

$$\Psi_3 = (5/6)^{1/2}s - (1/6)^{1/2}d_z$$

These are probably the bonds formed by silver in  $\text{Ag}(\text{CN})_2^-$  ( $4d5s5p$  bonds), which is known to be linear.<sup>5</sup> Here the  $s$  and  $d$  levels have nearly the same energy, with the  $p$  level higher.

#### Other types of bonds

It may occur that the  $s$  level, when it lies lowest, will be occupied by an unshared pair of electrons, and  $p$ - $d$  bonds will be formed. In order for  $p$ - $d$  bonds to be orthogonal, the angles between them must satisfy the equation:

$$\sin^2 \alpha \cos \theta + \frac{1}{2} \cos^2 \alpha (3 \cos^2 \theta - 1) = 0.$$

As in the case of the  $s$ - $p$ - $d$  bond, there are two angles for a given shape of bond. But, since there is only one shape parameter, these angles are not independent. The specification of one angle determines the shape and strength of the bond and also the other possible angle.

*Four  $p$ - $d$  bonds.* No more than four equivalent cylindrical  $p$ - $d$  bonds may be formed. The two configurations given on page 899, although quite strong, are poor sterically. It is to be expected that  $\text{SCl}_4$ , which probably has this type of bond, will form a non-cylindrical bond with better steric properties.

*Three  $p$ - $d$  bonds.* Three strongest bonds with a strength 2.828 can be formed at angles  $65^\circ 44'$  and  $144^\circ 12'$ . In the molecule  $\text{P}_4$  the phosphorus atoms may be bonded by  $p$  bonds or by  $p$ - $d$  bonds. In the former case the bond angle would tend to be  $90^\circ$  and the most probable configuration would place the four  $P$  atoms at the corners of a square, connected by alternate single and double bonds. The single bond functions have a strength of 1.732, while the double bonds have much less than twice the energy of a single bond. Much stronger  $p$ - $d$  bond functions can be formed if the  $P$  atoms are placed at the corners of a regular tetrahedron, with bond angles of  $60^\circ$ .

<sup>5</sup> J. L. Hoard, private communication

Bonds may be hindered from their tendency to form in the direction of the maximum of the bond function by steric or geometric factors, with an accompanying decrease in resonance energy. When this occurs, the bond function will rearrange itself so as to give a maximum strength in the new direction. The maxima of the rearranged bond functions will not lie in the directions of the bonds, but will generally assume positions between the bond directions and the directions of the undisturbed maxima. In this case, where the bonds tend to form at  $65^\circ 44'$  but are required by geometry to be at  $60^\circ$ , the maxima of the bond functions will be in directions  $64^\circ 02'$  apart, and their strength in the bond directions is 2.819. The bond functions are then

$$\begin{aligned}\Psi_1 &= 0.4520p_z + 0.3500p_x + 0.3593d_z + 0.2663d_x + 0.6880d_{x+z} \\ \Psi_2 &= 0.4520p_z - 0.1750p_x + 0.3031p_y + 0.3593d_z - 0.1332d_x - 0.2306d_{x+y} \\ &\quad - 0.3440d_{x+z} + 0.5958d_{y+z} \\ \Psi_3 &= 0.4520p_z - 0.1750p_x - 0.3031p_y + 0.3593d_z - 0.1332d_x + 0.2306d_{x+y} \\ &\quad - 0.3440d_{x+z} - 0.5958d_{y+z}.\end{aligned}$$

Where the bond directions are  $(35^\circ 16', 0^\circ)$ ,  $(35^\circ 16', 120^\circ)$ , and  $(35^\circ 16', 240^\circ)$ . The bonds are composed 32.67 percent of the  $p$  eigenfunctions. Bond functions with their maxima at  $60^\circ$  have a strength of only 2.773.

*Two p-d bonds.* Two bond functions may be formed at  $180^\circ$  with a strength of 2.806 as compared with the strongest bond functions at  $144^\circ 12'$  with a strength 2.828.

I wish to express my appreciation of the assistance of Professor Linus Pauling, at whose suggestion this problem was undertaken. I am also indebted to Dr. Boris Podolsky, now of Kharkov, for some of the rotation transformation formulas.

## APPENDIX I

### Problem

To construct the normalized bond function  $\Psi_j = \sum_{k=1}^m a_{jk} \psi_k$  with maximum value in the direction  $\theta_0$ ,  $\phi_0$  and orthogonal to  $n$  given orthogonal, normalized bond functions of the same type,

$$\Psi_i = \sum_{k=1}^m a_{ik} \psi_k \quad (i = 1, 2, 3, \dots, n) (j \neq i). \quad (1)$$

The orthogonality and normalization conditions require

$$\sum_{k=1}^m a_{ik} a_{lk} = \delta_{il} \quad (= 0 \text{ where } i \neq l; = 1 \text{ where } i = l). \quad (2)$$

Let

$$\Lambda = \sum_{k=1}^m a_{jk} \psi_k - \frac{\lambda}{2} \left[ \sum_{k=1}^m a_{jk}^2 - 1 \right] - \sum_{i=1}^n \sum_{k=1}^m \mu_i a_{ik} a_{jk} = \Psi_j \quad (3)$$

$\Psi_j$  will be a maximum when

$$\frac{\partial \Lambda(\theta_0, \phi_0)}{\partial a_{jk}} = 0 = \psi_k(\theta_0, \phi_0) - \lambda a_{jk} - \sum_{i=1}^n \mu_i a_{ik} \quad k = (1, 2, \dots, m). \quad (4)$$

Hence

$$a_{jk} = \frac{\psi_k(\theta_0, \phi_0) - \sum_{i=1}^n \mu_i a_{ik}}{\lambda}. \quad (5)$$

Multiplying this by  $a_{lk}$  ( $l \neq j$ ) and summing over  $k$  it is found that

$$\mu_l = \sum_{k=1}^m a_{lk} \psi_k = \Psi_l. \quad (6)$$

By squaring (5) and summing over  $k$  we get

$$\lambda = \left[ \sum_{k=1}^m \psi_k^2 - \sum_{i=1}^n \Psi_i^2 \right]^{1/2}. \quad (7)$$

Hence

$$a_{jk} = \frac{\psi_k - \sum_{i=1}^n a_{ik} \Psi_i}{\left[ \sum_{k=1}^m \psi_k^2 - \sum_{i=1}^n \Psi_i^2 \right]^{1/2}} \quad (8)$$

$$\Psi_j = \left[ \sum_{k=1}^m \psi_k^2 - \sum_{i=1}^n \Psi_i^2 \right]^{1/2} \quad (9)$$

### Corollary

When the  $m$  original eigenfunctions comprise only completed subgroups,

$$\sum_{k=1}^m \psi_k^2 = m \quad \text{and} \quad \Psi_j = \left[ m - \sum_{i=1}^n \Psi_i^2 \right]^{1/2}.$$

### APPENDIX II

*Proof that the most general  $d$  eigenfunction (arbitrarily oriented) is a linear combination of  $d_z$  and  $d_x$ .* The most general  $d$  eigenfunction is

$$\mathcal{D} = A d_x + B d_{x+y} + C d_{x+z} + D d_{y+z} + E d_z$$

which in Cartesian coordinates is

$$\mathcal{D} = 1/r^2 (a'x^2 + b'y^2 + c'z^2 + d'xy + e'xz + f'yz)$$

that is, the general quadratic. A rotation transformation will change the general quadratic to one containing squares only.

$$\mathcal{D} = 1/r^2 (ax^2 + by^2 + cz^2).$$

The coefficients are restricted by the fact that  $D$ , to be an eigenfunction, must satisfy Laplace's equation; and also must be normalized, so that

$$a + b + c = 0$$

$$\int_{\tau} D^2 d\tau = 4\pi.$$

The normalization equation when evaluated gives the relation

$$3(a^2 + b^2 + c^2) + 2(ab + ac + bc) = 15.$$

From the two relations we get

$$D = ax^2 - \frac{1}{2}(a \pm (15 - 3a^2)^{1/2})y^2 - \frac{1}{2}(a \mp (15 - 3a^2)^{1/2})z^2.$$

But this may be obtained from

$$D = a'd_x - (1 - a'^2)^{1/2}d_z$$

by setting

$$a = \frac{1}{2}(15)^{1/2}a' - \frac{1}{2}(5)^{1/2}(1 - a'^2)^{1/2}$$

### APPENDIX III

#### Problem

To determine the behavior of  $S$ ,  $P$ , and  $D$  under the general rotation transformation. If the coordinate axes are rotated for an angle  $\phi_d'$  about the  $z$  axis, then an angle  $\theta_d$  about the  $y$  axis, then again  $\phi_d$  about the  $z$  axis, the coordinates of the point  $P$ ,  $\theta'$  and  $\phi'$  appear as shown in Fig. 3, where all lines drawn are arcs of great circles.

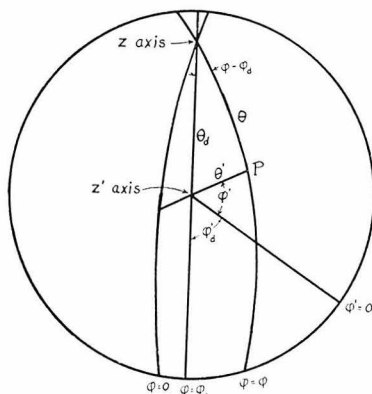


Fig. 3. Rotation of axes on the unit sphere.

By spherical trigonometry we have

$$\cos \theta' = \cos \theta_d \cos \theta + \sin \theta_d \sin \theta \cos (\phi - \phi_d)$$

$$\sin (\phi' + \phi_d') = \frac{\sin \theta \sin (\phi - \phi_d)}{\sin \theta'}$$

$$\cos (\phi' + \phi_d') = \frac{\cos \theta_d \sin \theta \cos (\phi - \phi_d) - \sin \theta_d \cos \theta}{\sin \theta'}.$$

We may easily solve these to get  $\sin \phi'$ ,  $\sin 2\phi'$ ,  $\cos \phi'$ ,  $\cos 2\phi'$  in terms of  $\theta$ ,  $\phi$ ,  $\theta_d$ ,  $\phi_d$ ,  $\phi_d'$ .

We also wish to evaluate

$$P_l^{[m]}(\cos \theta') = P_l^{[m]}[\cos \theta_d \cos \theta + \sin \theta_d \sin \theta \cos (\phi - \phi_d)].$$

This may be done by use of Gegenbauer  $C$  functions.\*

$$P_l^{[m]}(\cos \theta') = \frac{(2m)!}{2^m m!} \sin^m \theta' C_{l-m}^{m+1/2}(\cos \theta').$$

But:

$$\begin{aligned} C_{l-m}^{m+1/2}(\cos \theta_d \cos \theta + \sin \theta_d \sin \theta \cos (\phi - \phi_d)) &= \frac{\Gamma(2m)}{[\Gamma(m + \frac{1}{2})]^2} \times \\ &\sum_{\lambda=0}^{l-m} \left\{ \frac{(-1)^\lambda 2^{2\lambda} \Gamma(l-m-\lambda+1)}{\Gamma(l+m+\lambda+1)} [\Gamma(m+\lambda+\frac{1}{2})]^2 \times \right. \\ &\left. (2m+2\lambda) \sin^\lambda \theta_d \sin^\lambda \theta C_{l-m-\lambda}^{m+\lambda+1/2}(\cos \theta_d) C_{l-m-\lambda}^{m+\lambda+1/2}(\cos \theta) C_\lambda^m(-\cos(\phi - \phi_d)) \right\}. \end{aligned}$$

Making the following simplifications since  $l$ ,  $m$ , and  $\lambda$  are integers

$$\Gamma(n) = (n-1)!$$

$$\Gamma(n + \frac{1}{2}) = \frac{(2n)!}{2^{2n} n!} (\pi)^{1/2}$$

where  $n$  is an integer

$$\begin{aligned} C_{l-m-\lambda}^{m+\lambda+1/2}(\cos x) &= \frac{2^{m+\lambda} (m+\lambda)!}{(2m+2\lambda)! \sin^{m+\lambda} x} \\ C_\lambda^m(-x) &= (-1)^\lambda C_\lambda^m(x) \end{aligned}$$

we obtain

$$\begin{aligned} P_l^{[m]}(\cos \theta') &= \frac{m! 2^m \sin^m \theta'}{\sin^m \theta_d \sin^m \theta} \sum_{\lambda=0}^{l-m} \frac{(l-m-\lambda)!(m+\lambda)}{(l+m+\lambda)! m} \\ &\quad P_l^{[m+\lambda]}(\cos \theta_d) P_l^{[m+\lambda]}(\cos \theta) C_\lambda^{[m]}(\cos(\phi - \phi_d)). \end{aligned}$$

Using these formulas we get for our general expressions of eigenfunctions rotated through arbitrary angles

$$\begin{aligned} s &= P_0^0(\cos \theta') = 1 \\ p_z &= 3^{1/2} P_1^0(\cos \theta') = 3^{1/2} (\cos \theta_p \cos \theta + \sin \theta_p \sin \theta \cos(\phi - \phi_p)) \\ d_z &= 5^{1/2} P_2^0(\cos \theta') = \frac{1}{4} (5)^{1/2} \{ (3 \cos^2 \theta_d - 1)(3 \cos^2 \theta - 1) \} \end{aligned}$$

\* See Whittaker and Watson, "Modern Analysis", Chap. XV for most of the formulas involving the Gegenbauer function.

$$\begin{aligned}
& + 3 \sin 2\theta_d \sin 2\theta \cos (\phi - \phi_d) + 3 \sin^2 \theta_d \sin^2 \theta \cos 2(\phi - \phi_d) \} \\
d_x = & \frac{1}{12}(15)^{1/2}P_2^2(\cos \theta') \cos 2\phi' = \frac{1}{2}(15)^{1/2}\{ \sin^2 \theta \cos 2(\phi - \phi_d) \cos 2\phi_d' \\
& + \frac{1}{2}(3 \cos^2 \theta - 1) \sin^2 \theta_d \cos 2\phi_d' - \frac{1}{2} \sin^2 \theta \cos 2(\phi - \phi_d) \sin^2 \phi_d \cos 2\phi_d' \\
& + \sin^2 \theta \sin 2(\phi - \phi_d) \cos \theta_d \sin 2\phi_d' - \sin 2\theta \sin (\phi - \phi_d) \sin \theta_d \sin 2\phi_d' \\
& - \frac{1}{2} \sin 2\theta \cos (\phi - \phi_d) \sin 2\theta_d \cos 2\phi_d' \}.
\end{aligned}$$

By carrying the transformed  $p_z$  through a second rotation  $\phi_d'$ ,  $\theta_d$ ,  $\phi_d$  and expressing all angles  $\theta$  and  $\phi$  in terms of the original  $s$ ,  $p$ , and  $d$  eigenfunctions we arrive at the expression given in the text for the most general eigenfunction.

## The Crystal Structure of Sulvanite, $Cu_3VS_4$ .

By

Linus Pauling and Ralph Hultgren in Pasadena.

(With 3 figures.)

Massive sulvanite,  $Cu_3VS_4$ , from Burra Burra in Australia was recognized as cubic by Orceel<sup>1)</sup> and de Jong<sup>2)</sup> from its isotropic reflection of polarized light. De Jong prepared powder X-ray photographs of the substance, and assigned indices to the lines on the basis of a cubic unit with  $a_0 = 10.75 \text{ \AA}$ , containing 8  $Cu_3VS_4$ . Assuming chemically identical atoms to be crystallographically equivalent, he suggested a complicated arrangement of the atoms within this unit.

We noticed that the experimental data published by de Jong do not require such a large unit, but can be accounted for by a unit with  $a_0 = 5.375 \text{ \AA}$ , containing 1  $Cu_3VS_4$ , and we planned to study the crystal further. The opportunity to do this arose when a new find of sulvanite, from near Mercur, Utah, was made<sup>3)</sup>, consisting of cleavable masses and a few individual crystals. Dr. W. T. Schaller of the United States Geological Survey very kindly lent us this material, enabling us to prepare excellent Laue and oscillation photographs. Data from these show conclusively that the true unit contains only one molecule. A rigorous derivation has led to a very interesting new type of atomic arrangement.

### The unit of structure and space-group symmetry.

Several oscillation photographs were prepared of the radiation from a molybdenum-target tube, either unfiltered or filtered through zirconia, reflected from (100) of a crystal of sulvanite oscillating through  $45^\circ$  about a vertical [010] axis. A cleavage face about 2.5 mm. across and a smaller wellformed cube about 0.8 mm. on edge were used. Various orders of (100) up to (800) were observed to reflect, with the estimated relative intensities given in table I.

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1) J. Orceel, Bl. Soc. franç. Min. **51**, 205. 1928.

2) W. F. de Jong, Z. Krist. **68**, 522. 1928.

3) C. A. Schempp and W. T. Schaller, Am. Min. **16**, 557. 1931.



Table I.  
Oscillation data from (100) of sulfvanite.

X-ray Line	Wave Length	Order	Angle of Reflection	$d_{100}$	Estimated Intensity	Calculated Intensity for $u = 0.235$
$MoK\beta$	0.6311	1	$3^\circ 23'$	5.348		
$\alpha$	.7093	1	$3^\circ 47'$	5.365	5	37
$\gamma$	.6197	2	$6^\circ 38'$	5.361		
$\beta$		2	$6^\circ 45'$	5.371		
$\alpha_1$	.70783	2	$7^\circ 35'$	5.366	3	49
$\alpha_2$	.71212	2	$7^\circ 37'$	5.375		
$\beta$		3	$10^\circ 40'$	5.367		
$\alpha_1$		3	$11^\circ 24'$	5.371	0.8	4.0
$\alpha_2$		3	$11^\circ 28'$	5.370		
$\gamma$		4	$13^\circ 20'$	5.372		
$\beta$		4	$13^\circ 36'$	5.371		
$\alpha_1$		4	$15^\circ 17'$	5.371	10	53
$\alpha_2$		4	$15^\circ 23'$	5.368		
$\alpha_1$		5	$19^\circ 14'$	5.374		
$\alpha_2$		5	$19^\circ 22'$	5.370	1	7.4
		6			Absent	1.6
		7			Absent	0.5
		8			1	6.6

Weighted mean:  $d_{100} = \underline{5.370 \text{ \AA}}$ .

The value of  $a_0 = 5.370 \pm 0.005 \text{ \AA}$  (table I) was obtained from a photograph of radiation reflected on the same plate from (100) of sulfvanite and (0001) of  $\beta$ -alumina, for which a spacing of  $11.225 \text{ \AA}$  was assumed<sup>1)</sup>. This agrees well with the value  $\frac{1}{2} \times 10.750 = 5.375 \text{ \AA}$  from de Jong.

Laue photographs were prepared in the usual way from two small crystals (described by Schempp and Schaller), the incident beam being normal to (100), (110), or (111), or making small angles with the normals to these faces. On assigning indices to the reflections with the aid of gnomonic projections and calculating values of  $n\lambda$  on the basis of a unit with  $a_0 = 5.37 \text{ \AA}$ , it was found that none of the values was smaller than  $0.24 \text{ \AA}$ , the short wave-length limit of the incident radiation. Consequently there is no evidence requiring a larger unit of structure; and in view of the excellence of the Laue photographs obtained and the

1) Linus Pauling and A. Björkeson, Pr. Nat. Acad. Am. **11**, 445. 1925.

sensitivity of the Laue method of determining the true unit<sup>1)</sup>, the unit with

$$\underline{a_0 = 5.370 \text{ \AA}}$$

may be confidently accepted as the true one. With 1  $\text{Cu}_3\text{VS}_4$  in the unit, the calculated density is 3.94 g./cm<sup>3</sup>, in satisfactory agreement with the reported values<sup>2)3)</sup> 3.98, 4.01, and 4.03.

Many observed reflections eliminate the body-centered and face-centered lattices, requiring the lattice to be simple cubic. Laue photographs through (100), (110), and (111) show the symmetry elements expected for  $O$ ,  $T_d$ , and  $O_h$ , rather than  $T$  and  $T_h$ . (It may be mentioned that photographs showing a fourfold and a three-fold axis were obtained from the same crystal, which is thus proved to be cubic.) The possible space groups are thus limited to  $T_d^1$ ,  $T_d^4$ ,  $O^1$ ,  $O^2$ ,  $O^6$ ,  $O^7$ ,  $O_h^1$ ,  $O_h^2$ ,  $O_h^3$ , and  $O_h^4$ . The observed reflections (100), (300), and many others eliminate  $T_d^4$ ,  $O^2$ ,  $O^6$ ,  $O^7$ ,  $O_h^2$ ,  $O_h^3$ , and  $O_h^4$ , leaving only  $T_d^1$ ,  $O^1$ , and  $O_h^1$ . These three space groups are indeed the only ones which provide positions for the atoms  $V$ , 3  $\text{Cu}$ , 4  $S$  in a cubic unit.

The space groups  $O^1$  and  $O_h^1$  provide the possible positions

$$\begin{aligned} 1a. & \quad 000 \\ 1b. & \quad \frac{1}{2}\frac{1}{2}\frac{1}{2} \\ 3a. & \quad 0\frac{1}{2}\frac{1}{2}, \quad \frac{1}{2}0\frac{1}{2}, \quad \frac{1}{2}\frac{1}{2}0 \\ 3b. & \quad \frac{1}{2}00, \quad 0\frac{1}{2}0, \quad 00\frac{1}{2} \end{aligned}$$

for the atoms in the unit. For any atomic arrangement based on these positions the structure factor becomes  $F = f_V + 3f_{\text{Cu}} + 4f_S$  for all even order reflections, which should consequently show a normal decline in intensity with decreasing interplanar distance. The observation that (400) reflects more strongly than (200) consequently eliminates all such arrangements. The space group is hence determined to be

$$\underline{T_d^1 - P \bar{4}3 m.}$$

### The atomic arrangement.

The possible atomic positions provided by  $T_d^1$  are 1a, 1b, 3a, 3b, and, in addition,

$$4a. \quad uuu, \quad u\bar{u}\bar{u}, \quad \bar{u}u\bar{u}, \quad \bar{u}\bar{u}u.$$

1) Illustrated, for example, by the work of R. G. Dickinson, J. Am. chem. Soc. **45**, 958. 1923; Z. Krist. **64**, 400. 1926, on tin tetraiodide, and of Linus Pauling and L. O. Brockway, Z. Krist. **82**, 188. 1932, on chalcopyrite.

2) G. A. Goyder, J. chem. Soc. London **77**, 1094. 1900.

3) H. Schultze and H. Steinmetz, Z. Krist. **49**, 40. 1911.

The sulfur atoms are shown by the fore-going argument to occupy 4a. The vanadium atom may be placed in 1a rather than 1b without loss of generality. Two distinct structures are then obtained by placing 3  $Cu$  in 3a or in 3b. These are the only possible atomic arrangements.

It is easily shown that the observed intensities of reflection in various orders from (100) require that for the first of these two arrangements the parameter lie in the neighborhood of  $\frac{1}{4}$ ; at  $u = 0.27 \pm 0.02$  the best agreement is obtained, though this is not very good, the observed rather strong first-order reflection not being well accounted for. This arrangement is a very simple and reasonable one, obtained from the sphalerite arrangement by replacing one of the zinc atoms by vanadium and the other three by copper. The approximation of the value of  $a_0$  to that for sphalerite, 5.42 Å, further suggests this structure. Chalcopyrite,  $CuFeS_2$ , has been shown<sup>1)</sup> to have a structure similarly related to that of sphalerite. Despite its reasonableness, however, this is not the structure of sulfanite, for many intensity comparisons on Laue photographs are incompatible with this atomic arrangement. For example, (643) is observed to reflect on Laue photographs about as intensely as (553), whereas the calculated intensity of reflection of (553) is over ten times that of (643) throughout the parameter range  $0.20 < u < 0.30$ . It is, indeed, evident from the nature of the photographs that the structure of sulfanite is not closely related to the sphalerite structure; for inasmuch as the  $f$ -values for  $V$  and  $Cu$  are not very different, reflections other than those with  $h, k, l$  either all odd or all even should be very weak (as was the case in chalcopyrite, where such reflections were not observed at all in the first two investigations of this crystal and appeared only as very weak Laue spots in the last study<sup>1)</sup>), whereas actually on the sulfanite Laue photographs the strongest reflections are those from planes not satisfying this condition.

The parameter for the remaining structure, with 3  $Cu$  in 3b, can be limited to a narrow range of values with the aid of intensity comparisons on oscillation and Laue photographs. In Fig. 1 there are plotted the intensities of reflection in various orders from (100) for the parameter range 0.20 to 0.30 (limitation to this region being easily made) calculated from the equation

$$I_{n00} = \text{Constant} \cdot n \cdot \frac{1 + \cos^2 2\theta}{2 \sin 2\theta} \cdot \{f_{0V} + f_{0Cu} (2 + \sqrt{-1})^n + 4 f_{0S} \cos 2\pi n u\}^2 \cdot e^{-0.125 \cdot d_{n00}^2} \quad (4)$$

1) Linus Pauling and L. O. Brockway, Z. Krist. **82**, 188. 1932.

The factor  $n$  is required by the experimental conditions, under which the amount of incident radiation intercepted by the face of the crystal increases linearly with the order of reflection. The temperature factor corresponds to an estimated characteristic temperature of about  $530^\circ$ . The  $f_0$ -values used are those of Pauling and Sherman<sup>1</sup>). It is seen that the observed intensity relations  $(800) \gg (600)$  and  $(500) > (300)$  limit  $u$  to between 0.223 and 0.239, the quantitative agree-

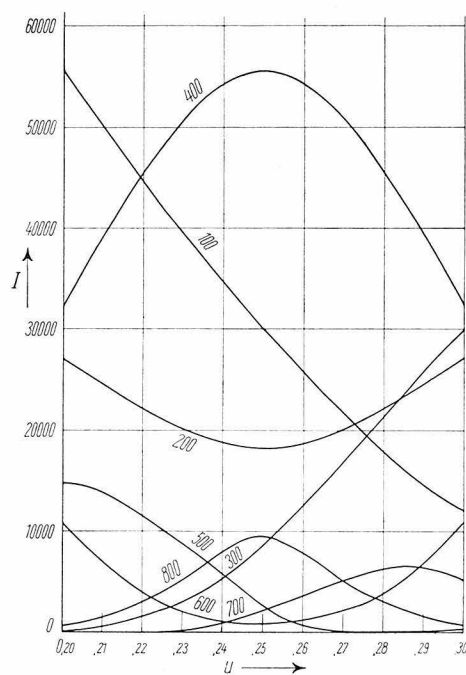


Fig. 1.

Fig. 1. Calculated intensities for various orders of reflection from (100) of sulvanite as functions of  $u$ .

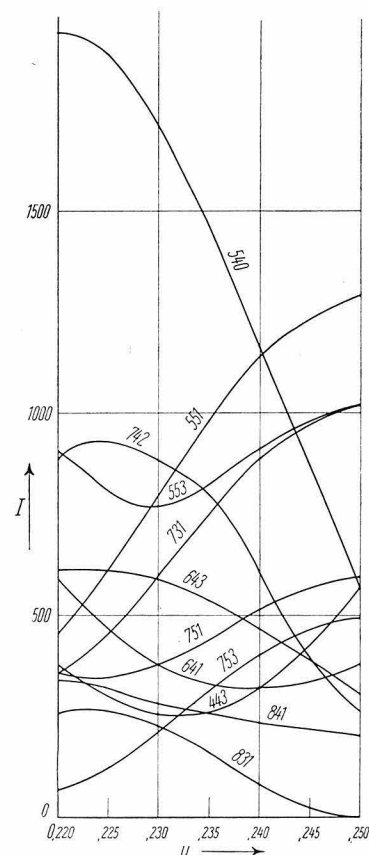


Fig. 2.

Fig. 2. Calculated intensities of Laue reflections.

ment being most satisfactory in the neighborhood of 0.235. The intensity relation  $(731) > (643)$  on Laue photographs further requires that  $u$  be greater than 0.230, as is seen from Figure 2, in which there are plotted some intensity curves calculated for a wave-length of  $0.40 \text{ \AA}$  with the expression

1) Linus Pauling and J. Sherman, Z. Krist. **81**, 1. 1932.

$$I_{hkl} = \text{Constant} \cdot \frac{1 + \cos^2 2\theta}{2 \sin 2\theta} |F_{0hkl}|^2 e^{-0.125 d_{hkl}^2} \quad (2)$$

with  $F_0 = \sum_j f_{0j} e^{2\pi i(hx_j + ky_j + lz_j)}$ .

(The use of Lorentz and polarization factors not corresponding exactly to the Laue technique probably introduces no appreciable error.) The parameter accordingly has the value

$$u = 0.235 \pm 0.004.$$

The agreement between observed and calculated intensities is shown in Tables I and II.

Table II.  
Data from Laue photographs 4 and 6.

Laue 4. Incident beam  $8^\circ$  from [110]

Laue 6. Incident beam  $2^\circ$  from [110]

$hkl$	$d_{hkl}$	Calculated Intensity for $u = 0.235$	Observed Intensity Laue 4		Observed Intensity Laue 6	
211	2.19 Å	6	2.5 at $\lambda = 0.44$ Å			
221	1.79	63	25	.40		
311	1.62	126	15	.28		
320	1.53	60			25 at $\lambda = 0.39$ Å	
321	1.44	2	0.4	.41		
322	1.30	11	1.0	.30	12	.38
331	1.23	60	5	.30		
421	1.17	13	5	.42	13	.39
332	1.15	2			0.5	.39
430	1.07	5			3.5	.37
431	1.05	3	0.4	.36	0.5	.35
510	1.05	0	0.0	.32		
432	1.00	18	2.5	.35		
520	1.00	2	0.3	.38		
441	0.94	10	1.5	.44		
433	.92	2	0.1	.39		
531	.91	23	3.5	.37	10	.38
611	.87	4			0.7	.40
540	.84	15	1.4	.40		
443	.84	3	0.4	.39		
533	.82	14			7	.40
542	.80	1			0.3	.37
632	.77	2	0.4	.42	0.5	.42
551	.75	10	1.0	.43		
711	.75	10	0.6	.35		

Table II (continuation).

$hkl$	$d_{hkl}$	Calculated Intensity for $u = 0.235$	Observed Intensity Laue 1		Observed Intensity Laue 6	
641	.74	3	0.3	.38	0.7	.41
720	.74	13	0.7	.37		
553	.70	8	0.6	.37		
643	.69	5	0.4	.39	1.0	.41
652	.68	7	0.3	.37	0.7	.37
733	.66	6			0.5	.42
742	.65	8	0.4	.39	0.6	.37
821	.65	2	0.1	.36		
830	.63	1	0.05	.39		
831	.63	2			0.2	.40
751	.62	4			0.4	.42
841	.60	2			0.3	.41
753	.59	3			0.3	.39

### Description of the structure.

The atomic arrangement found for sylvanite is a new type, shown in Figure 3. Each copper atom is surrounded by four sulfur atoms at the corners of a nearly regular tetrahedron. Each vanadium atom is surrounded by four sulfur atoms at the corners of a regular tetrahedron. Each sulfur atom is surrounded by three copper atoms at three of the corners of a nearly regular tetrahedron, and a vanadium atom not at the fourth corner of the tetrahedron, but in the negative position to this; that is, in the pocket formed by the three copper atoms.

It is probable that there are bonds of essentially covalent type between each atom and its four nearest neighbors. The mutual orientation of the four sulfur bonds is very surprising; for in all other sulfur-containing covalent crystals whose structures are known with certainty, such as  $ZnS$ ,  $MoS_2$ ,  $FeS_2$ , etc., the sulfur bonds are at approximately tetrahedral angles. It is true, however, that other angles may be expected on theoretical grounds, inasmuch as the 3d as well as 3s and 3p orbital wave functions may take part in bond formation<sup>1)</sup>, in which case bonds at  $110^\circ$  and  $71^\circ$  may well be formed. The factors determining the stability of such bonds rather than tetrahedral bonds are not known. The following argument suggests that electrostatic interactions may be important in stabilizing the sylvanite structure. If each of the atoms in sylvanite forms four extreme covalent bonds, each consisting of two electrons

1) See R. Hultgren, *Physic. Rev.* **40**, 891. 1932.

shared equally between two nuclei, then the average electric charges on the various atoms will correspond to the formula  $Cu_3^- V^+ S_4^{++}$ . In the sulfanite structure the ions immediately adjacent to each ion are the same as in the sphalerite-type structure discussed above and eliminated by the X-ray data. In the next sphere of influence, however, there is a difference; in the sulfanite structure six of the negatively charged copper

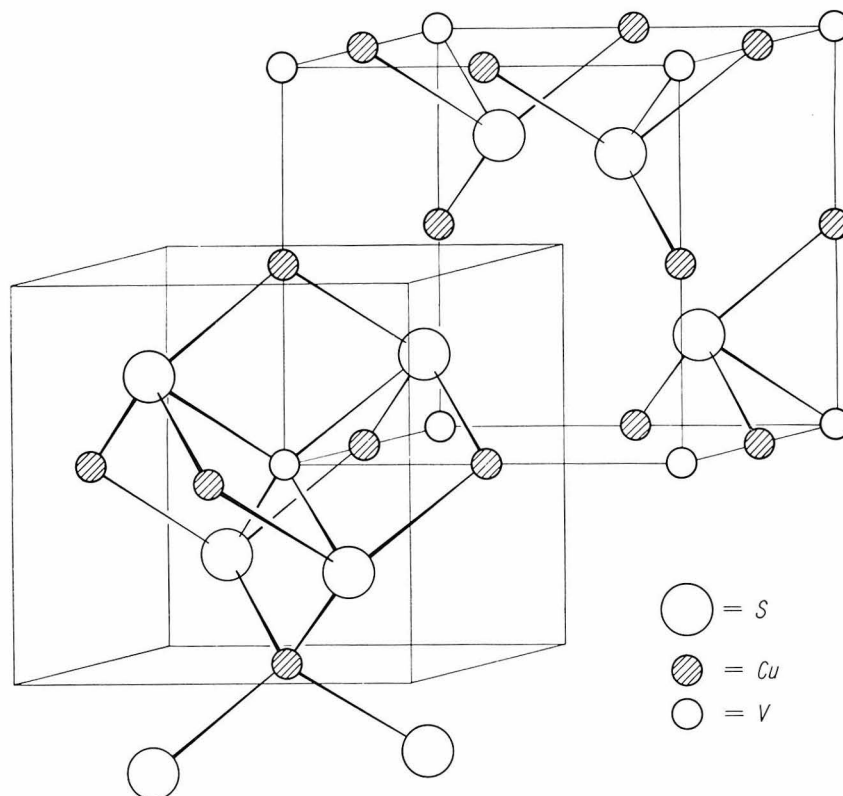


Fig. 3. The atomic arrangement in sulfanite,  $Cu_3VS_4$ .

atoms are brought to within  $\frac{1}{2}a_0$  of each positively charged vanadium atom, with a resultant stabilization of the structure because of the Coulomb terms. This is shown by the Madelung constants, which have the values 39.217174 for  $Cu_3^- V^+ S_4^{++}$  with the sulfanite structure and 37.026993 for the sphalerite-type structure (each for  $u = \frac{1}{4}$ , and referred to  $a_0$ ), corresponding to an energy difference of 135 kcal/mole in favor of the sulfanite structure. This consideration is, of course, too idealized, for the bonds without doubt have considerable ionic character, which

operates in such a direction as to make the metal atoms more positive and the sulfur atoms more negative<sup>1</sup>). If this occurs to the extent indicated by the formula  $Cu_3^- V^{++} S_4^+$ , the Madelung constants become 17.249703 and 14.329462, respectively, the sulfanite structure being then favored by the energy difference 180 kcal/mole. Only if the ionic character were to become so pronounced as to make the copper atoms positive would the Madelung constant for the sulfanite structure fall below that for the sphalerite-type structure.

The interatomic distances found are  $V-S = 2.186 \pm 0.040$  Å and  $Cu-S = 2.285 \pm 0.014$  Å. The  $Cu-S$  distance is somewhat smaller than the sum of the tetrahedral radii<sup>2</sup>) for sulfur and univalent copper, 2.39 Å. As in the case of chalcopyrite, this probably indicates that the valence states are not well defined as  $Cu_3^I V^V S_4$ , but fluctuate, the copper resonating between cuprous and cupric states and the vanadium between quinquivalent and lower states.

### Summary.

The study by means of Laue and oscillation photographs of the cubic mineral sulfanite, using single crystals from Mercur, Utah, has shown the unit of structure to have  $a_0 = 5.370 \pm 0.005$  Å, and to contain 1  $Cu_3VS_4$ . The space group is  $T_d^1-P\bar{4}3m$ . The atomic arrangement is a new type,  $V$  at 000, 3  $Cu$  at  $\frac{1}{2}00$ ,  $0\frac{1}{2}0$ ,  $00\frac{1}{2}$ , and 4  $S$  at  $uuu$ ,  $u\bar{u}\bar{u}$ ,  $\bar{u}u\bar{u}$ ,  $\bar{u}\bar{u}u$ , with  $u = 0.235 \pm 0.004$ . Smallest interatomic distances are  $V-S = 2.186 \pm 0.040$  Å, and  $Cu-S = 2.285 \pm 0.014$  Å.

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1) For a discussion of ionic character of covalent bonds see Linus Pauling, Pr. Nat. Acad. Am. **18**, 414, 1932; J. Am. chem. Soc. **54**, 3570, 1932.

2) Linus Pauling and M. L. Huggins, Z. Krist. to be published.